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Hydrogen and Sulfur from Hydrogen Sulfide II.

Ambient Temperature Electrolysis Using Oxidation

of Hydrogen Sulfide by Air as the Prime Energy Source

by

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HYDROGEN AND SULFUR FROM HYDROGEN SULFIDE II.

AMBIENT TEMPERATURE ELECTROLYSIS USING OXIDATION OF

HYDROGEN SULFIDE BY AIR AS THE PRIME ENERGY SOURCE

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Abstract. Hydrogen sulfide recovered from the sweetening of fossil fuels or sought as a mineral for its intrinsic value might be converted, in an electrolytic process which uses atmospheric oxygen, into pipeline pressure hydrogen and sulfur. Such a process may be an alternative to the Claus Process, which recovers only sulfur and uses the hydrogen wastefully. It is also suggested that electrolysis provides a mechanism by which other gaseous products, as well as hydrogen, may be brought to pipeline pressures easily.

1. INTRODUCTION

Hydrogen sulfide, an industrial waste, is recovered in large quantities from the sweetening of fossil fuels. In 1979, 1.76 x 10^6 tons of sulfur were recovered from natural gas, and 2.31 x 10^6 tons were recovered from petroleum in the United States. In Canada, 6.1 x 10^6 tons were recovered,[1] mostly as hydrogen sulfide. Hydrogen sulfide has a moderately high heating value, 16.55 kJ/g if it is burned to sulfur dioxide and liquid water.[2] But its use as a fuel would be wasteful of sulfur as well as being environmentally unacceptable. Nevertheless, it is plentiful in nature; it should not be overlooked as a potentially valuable resource.†

The Claus process is now most widely used to dispose of H_2S. In this process, sulfur is recovered and the hydrogen is oxidized to water to furnish low-grade process heat.[3] The heating value of the hydrogen thus used is, on an annual basis, equivalent to that of 17 x 10^6 bbl of gasoline.[4] Alternatively, it could be used to hydrogenate one million tons of coal to produce 59 x 10^6 bbl of high-grade liquid hydrocarbon fuel, about 3% of the number of barrels of petroleum imported into the U.S. in 1980, or to produce about 3 x 10^6 metric tons of ammonia. If H_2S were sought as a resource, its contribution could be substantially higher.

In a previous paper,[4] we noted that, although we are most intrigued by the use of solar energy to effect the separation and

†Jon Noring, presently with the Sandia Livermore Laboratory, first emphasized this fact to the author.

recovery of both H_2 and S_x as well as the concommitant storage of solar energy. Electrolysis of H_2S and subsequent use of the resulting H_2 with atmospheric O_2 in a fuel cell to provide electric power for electrolysis is an interesting option which deserves consideration. We describe how the idea might be implemented, point out some interesting ramifications which may have general applicability to other systems, and present the results of some simple calculations.

2. THERMODYNAMICS OF IDEAL ELECTROLYTIC AND FUEL CELLS

The emf required to electrolyze a substance in a reversible electrolytic cell, or the emf produced by a chemical reaction which occurs within a reversible fuel cell, is given by the Nernst equation[5]

$$E = \pm \Delta G/nF, \qquad (1)$$

where E is the emf of the cell, ΔG is the change in the Gibb's function for the overall reaction which occurs in the cell, n is the number of moles of electrons transfered in the external circuit during the course of the reaction, and F is the Faraday constant. The + sign applies if one is dealing with an electrolysis cell; the - sign applies if one is dealing with a fuel cell.

The change in Gibb's function of a chemical reaction,

$$\Sigma a_i M_i = 0, \qquad (2)$$

where M_i is a reactant or product and a_i is its coefficient in

The margin handwriting: "Capital Pi, Product closure subscript i" roughly.

the chemical equation, is given in good approximation by

$$\Delta G = \Delta G^O + RT \ln \Pi P_i^{a_i}, \qquad (3)$$

where P_i is the fugacity of gaseous species i, assumed here to be ideal and therefore equal to its pressure and is very nearly 1 for condensed species and set equal to 1 for condensed species in this paper.
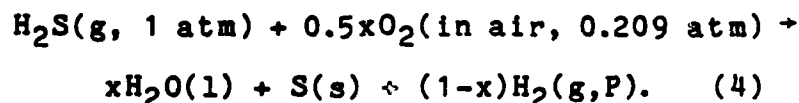
3. THE IDEALIZED PROCESS

Hydrogen-oxygen fuel cells are well known.[6] A patent,[7] which makes use of electrolysis for the production of H_2 and S_x from H_2S, exists. It is easy to imagine a coupling in which H_2 and S_x are produced from H_2S in an electrolysis cell, the electric power for which is provided by an H_2-O_2 fuel cell which uses part of the H_2 from the electrolysis cell and atmospheric O_2 as its reactants. It is not difficult to imagine various arrangements of mechanical components by means of which the process might be effected. One intriguing feature of the process is that, once H_2S has been introduced into the cell at its operating pressure in a suitable electrolyte, electrolysis can supply the work of pumping the H_2 to an arbitrarily high pressure (a pipeline pressure, for example) without the need for a mechanical gas-pumping device of any kind.

The thermodynamics of the reversible process is simple and straightforward. A schematic representation of the process is given in Fig. 1. The temperature for our example is 298.15 K. The

overall reaction, as can be seen by reference to Fig. 1, is

$$H_2S(g, \text{1 atm}) + 0.5xO_2(\text{in air, 0.209 atm}) \rightarrow$$
$$xH_2O(1) + S(s) \leftrightarrow (1-x)H_2(g,P). \quad (4)$$

If P and x in Eq. (4) are chosen so that $\Delta G = 0$,

$$(1-x)RT\ln P + x\Delta G^0_{H2O} - 0.5xRT\ln 0.209 - \Delta G^0_{H2S} = 0. \quad (5)$$

Equation (5) may be used to calculate the fraction of the H_2 in H_2S which must be used to effect the electrolysis and compress the remaining H_2 to pressure P in a reversible device. The results are given in Fig. 2, which shows the fraction of H_2 which must be used up, as well as that which remains for storage, as a function of the storage pressure. Figure 2 also shows the fraction of the H_2 which is used solely to perform pump work. It is noteworthy that only a tiny fraction of the H_2 need be sacrificed to bring the remainder to very high pressures, an observation that suggests that electrolytic pumping may have applicability to a great many processes in which a gaseous product, which is to be produced by electrolysis of a condensed phase, is wanted at a high pressure. It suggests that the often wasteful and inefficient process of compressing large volumes of gases may be replaced by pumping liquids first or by using batch processes in which the the system, originally at low pressure, is quickly brought to a high pressure by evolution of an electrolytically generated gas from a liquid solution, followed by collection of the gas at high pressure.
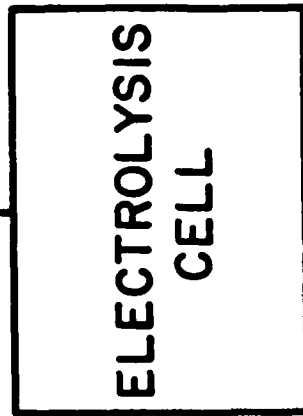
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FIGURE CAPTIONS

Fig. 1.   Schematic representation of the device. Hydrogen sulfide from a source at 1 atm is introduced into the electrolytic cell, which produces H_2 and S_x at some higher pressure P. In practice, the H_2S might be pumped into the electrolysis cell as a liquid or gas or in solution in an appropriate solvent. For our purpose, it is only necessary to note that it has become available to us at 1 atm and that our analysis need not consider the details of the mechanisms by which the components of the system operate. A fraction x of the H_2 at pressure P is fed to the fuel cell, and the rest is stored. Hydrogen at pressure P and O_2 at 0.209 atm[8] are the reactants in the fuel cell, which rejects liquid water at 1 atm.

Fig. 2.   Variation with storage pressure of the fraction of H_2 consumed, stored, and used to provide the work of compressing that which is stored.
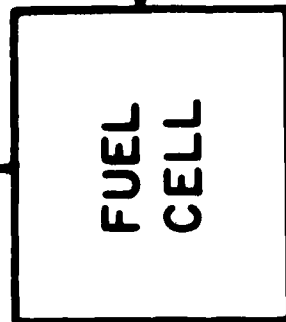
ELECTRICAL WORK

FUEL
CELL

$\frac{x}{2}O_2\left(\begin{array}{c}\text{from air, g}\\ \text{0.209 atm}\end{array}\right)$

$H_2O(l)$

$xH_2(g,P)$

ELECTROLYSIS
CELL

$(1-x)H_2(g,P)$
TO STORAGE

$S(s)$
TO STORAGE

$H_2S(g, 1\,atm)$

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